EXTRACTION PERFORMANCE STUDY OF GAHARU USING MICROWAVE EXTRACTION METHOD

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ABSTRACT

Nowadays, as technology develops, more process and equipments is found in order to extract gaharu especially for its essential oil. In producing high yield of essential oil with less time consuming, this study is important so that the extracted product can be used in multiple ways as in varies industry and are suitable for pharmaceutical and herbs industry. This study is limited to two parameters which are days of gaharu soaking and the microwave power. The gaharu grade C used will be grind and soak in the distilled water before extract and the oil yield will be analyze using Fourier transform infrared spectroscopy (FTIR). From this study, it have been proven that microwave extraction is suitable in extracting gaharu with acceptably low time comparing to other extraction equipment but the yield is too little and as gaharu itself contains low resin in it, the oil extracted were mostly visible at the wall of equipments. As the power of microwave increases, the yield obtained increases too due to the loosening of cell wall of gaharu that increase the yield essential oil. The days of soaking has also been proven to be directly proportional to the yield of oil extracted, considering the power of microwave set and other condition.From the analysis done by FTIR, several compounds have been found such as sulfoxide, alkanes, alkyl halides, alcohol and imines. Although the component of gaharu itself can't be ascertain, the existence of alcohol in some of the mixture shows that there might be possibilities of the chemical compound of gaharu such as jinkoh-eremol, agarospirol and jinkohol that were OH group miscible in the distilled water analyze.

ABSTRAK

Pada masa kini, dengan berkembangnya teknologi, pelbagai proses dan peralatan telah dijumpai untuk mengestrak gaharu terutamanya untuk mendapatkan minyak pati. Dalam menghasilkan hasil yang tinggi minyak pati dengan mengambil masa yang kurang, kajian ini adalah penting supaya produk yang diekstrak boleh digunakan dalam pelbagai industri dan sesuai untuk industri farmaseutikal dan herba. Kajian ini terhad kepada dua parameter yang merupakan hari gaharu direndam dalam air suling dan kuasa gelombang mikro yang digunakan. Gaharu gred C yang digunakan akan dikisar dan direndam di dalam air suling sebelum diekstrak dan hasil minyak akan dianalisis menggunakan inframerah spektroskopi jelmaan Fourier (FTIR). Dari kajian ini, ia telah membuktikan bahawa pengekstrakan gelombang mikro yang sesuai dalam mengeluarkan gaharu dengan masa rendah berbanding dengan lain-lain peralatan pengekstrakan tetapi menghasilkan minyak yang terlalu sedikit dan oleh kerana gaharu itu sendiri mengandungi resin yang rendah di dalamnya, minyak yang diekstrak kebanyakannya hanya dapat dilihat di dinding peralatanApabila kuasa mikro yang ditetapkan meningkat, hasil yang diperolehi meningkat. Ini disebabkan oleh dinding sel gaharu yang telah lemah menyebabkan minyak pati yang terhasil meningkat. Hari gaharu direndam juga telah terbukti berkadar terus dengan hasil minyak diekstrakDaripada analisis yang dilakukan oleh FTIR, beberapa sebatian telah dijumpai seperti sulfoxide, alkana, alkil halida, alkohol dan imines. Walaupun komponen gaharu itu sendiri tidak boleh ditentukan, kewujudan alkohol di beberapa campuran menunjukkan bahawa mungkin ada sebatian kimia gaharu seperti jinkoh-eremol, agarospirol dan jinkohol dalam kumpulan OH yang larut dalam air yang telah dianalisis.

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LIST OF SYMBOLS

m	Gradient
^{o}C	Degree
g	Gram
atm	Atmosphere
W	Watt

LIST OF ABBREVIATIONS

FTIR	Transform Infrared Spectroscopy
MAE	Microwave Assisted Extraction
SCFE	Supercritical extraction method

CHAPTER 1

INTRODUCTION

1.1 PROBLEM STATEMENT

Gaharu is a resin product which is produced by particular product and has a certain high commercial value but is threatened to extinction due to uncontrolled exploitation (Tarjuman M., 2011). It has at least 300 year in the Middle East, China and Japan and is used by Traditional Chinese, Unanai, Ayuravedic, and Tibetan physicians. They are used for the purpose of medical, which is the remedy for nervous system disorders such as neurosis, and exhaustion (Robert *et al*, 2004). There are many grades of agarwood, and the highest quality of the wood is extremely expensive. As a matter of fact, the first-grade wood is one of the most expensive natural products in the world, with prices of up to $13,000 per pound (Eden Botanicals, 2007).

Nowadays, though the Agarwood is also used for medical purpose, but as technology develops, more process and equipments is found in order to extract it, especially for its essential oil. However, throughout the year, there were still problems in extracting gaharu. As the goal is to obtain high yield of gaharu essential oil with reasonably low time in producing it, many equipment have been build and develop. Compared to other conventional method used such as ultrasonic assisted steam distillation by Ahmad Junaidy Jaapar 2008, the condition of high ratio of gaharu-water (1:20) and long extraction hour (9h) will be solved in this experiment by using microwave extraction.

By using microwave extractor to extract the gaharu, the extraction time is shorten and the reaction will consume less solvent (Jain T. *et al*, 2009). As no residue generated and no/small quantity water or solvent is use in the extractor, cleaner feature gives an advantages as there will be no risk that there will be impurities in the reaction.

1.3 RESEARCH OBJECTIVE

The objectives of this study are to study the performance of microwave extraction in extracting gaharu essential oil and the effects of microwave power, and days of gaharu soaked in distilled water to the yield extracted.

1.3 SCOPE OF THE STUDY

Extraction time, gaharu sizes, days of soaking, and the condition of the microwave extractor such as power, temperature and pressure are the parameters that can be manipulated in studying the performance of microwave extraction for extracting essential oil. However, this study is limited to two parameters which are days of gaharu soaking and the microwave power.

1.4 RATIONALE AND SIGNIFICANCE

In producing high yield of essential oil with less time consuming, this study is important so that the extracted product can be used in multiple ways as in varies industry and productions such as perfume, incense and in medicine. In the same time the study can suggest better extraction method, by which means the extraction time is short and that it produce reasonably amount of essential oil. The product yielded is also a fine chemical produced, as it is in high quality, which is suitable for pharmaceutical industry, as well as herbs industry. Increasing efficiency will increase the rate of profit gain from the manufacturing and processing of the essential oil. In particular, the study will help Malaysian Herbs Industry in producing more quality product.

CHAPTER 2

LITERATURE REVIEW

2.1 GAHARU

2.1.1 Gaharu

Gaharu or Agarwood is the resin-impregnated wood that is derived from the Aquilaria species of the family of Thymalaeacea. There are many names given for this resinous wood, including agar, agarwood, aloeswood, kalamabak and eaglewood (Angela.B et al. 2003). Other names such Eaglewood, Aloes Wood and Agalocha is also used (Broad, 1995) but it is commonly referred to as Gaharu in Malaysia. Agarwood is a large evergreen tree growing over 15-30 m tall and 1.5-2.5 m in diameter, and has white flowers (Chakrabarty et al., 1994). It is well known for its unique fragrant and highly valuable non-timber products in Asian tropical forest. The odor of Agarwood is complex and pleasing with few or no similar natural analogues.

The formation of agarwood occurs in the trunk and roots of trees are due to the infection by a parasite ascomycetous mould, Phialophora parasitica, a dematiaceous (dark-walled) fungus. The trees occasionally begin to produce an aromatic resin in response to this attack. As the fungus grows the resin dramatically increases the mass and density of the affected wood, changing its color from pale beige to dark brown or black within the heartwood (Ng et al., 1997). The oldest of the cultivated trees containing the oleoresin are 12 years of age whereas the resin found in wild harvested trees has been developing for 30 years or more. So the age of the raw material has a lot to do with the richness and complexity of the resin produced therein. However, there are many merits in the oil from the cultivated trees (Ng et al., 1997).

Figure 2.1: Picture of gaharu.

Table 2.1: Common Names of Agarwood

Language	Names
English	Agarwood, Aloeswood, Eaglewood
French	Bois d'aigle, Bois d'aloes
Vietnamese	Tram Huong
Chinese	Chen-xiang
Japanese	Jinkoh
Arabic	Oud
Indonesian	Gaharu
Malay	Gaharu
Thai	Kritsana noi

Source: Gaharu Online, n.d.

2.1.2 Distribution by country and habitat

The species of gaharu has a wide distribution, being found in Bangladesh, Bhutan, India, Indonesia, Malaysia, Myanmar, the Philippines, Singapore and Thailand. (Review of significant trade, 2003). Around the tropical region there has been reported that 15 species of Aquilaria has exists in India, Burma, China, Myanmar and Malaysia region. In Malaysia there are 5 species of Aquilaria found which are Aquilaria Hirta, Aquilaria Malaccensis, Aquilaria Rostrata, Aquilaria Microcorpa and Aquilaria Becanana. A significant number of research studies have been conducted on Aquilaria malaccensis (Ng et al., 1997) which is well distributed throughout Peninsular Malaysia except for Kedah and Perlis.

Five species of Aquilaria are recorded for Peninsular Malaysia and all are believed to be able to produce oleoresins (Cheng et al.2001)as shown in Table 2.2;

Table 2.2: gaharu producing species of Aquilaria in Peninsular Malaysia (Chang *et al*,2001)

Species	**Local name for resinous wood**	**Grade**
A.Malaccensis	Gaharu	Medium
A.microcarpa	Garu	
A.hirta	Chandan	Medium
A.rostrata	-	-
A.beccariana	Gaharu, tanduk	-

It has also been said that in peninsular Malaysia, Orang Asli has been the traditional harvester of gaharu and that in east Malaysia, Penans people are the traditional gatherers of gaharu (Hansen, 2000).

2.1.3 Physical properties

Chemical profile for each grade such as grade A, B and C were different. In peninsular Malaysia, the gaharu were mostly made of grade C quality (Chang et al., 2002). Different chemical component in gaharu oil will determine the characteristic or quality of the gaharu. Gaharu can be distinguished by colors, specifically 'reddish brown' and 'greenish brown' (Fatmawati Adam et al, 2005).

Table 2.3: Physical properties of Agarwood oil (sensibly depend on species of Aquilaria tree, mainly for color, odor, viscosity and specific gravity).

Properties	**Description**
Odor	sweet aromatic scent
Appearance	Lightly yellow to brownish liquid
Specific gravity (@25oC)	0.89 - 1.08 g/cm^3
Refractive index (@20^{o}C)	1.4910 - 1.6090
Optical Rotation (@20^{o}C)	-13.2o until -17.80
Acid value	6.8 -13.2
Ester value	18.3 - 27.1
Solubility	soluble in alcohol

2.1.4 Importance/uses

2.1.4.1 Medicine

Agarwood has been used for medicinal purposes for thousands of years, and continues to be used in Ayurvedic, Tibetan and traditional East Asian medicine (Chakrabarty et al., 1994; Fratkin, 1994). The Sahih Muslim, which dates back to approximately the eighth century, refers to the use of agarwood for the treatment of pleurisy and its use is referenced in the Ayurvedic medicinal text the Susruta Samhita. Agarwood is prescribed in traditional East Asian medicine to promote the flow of qi', to relieve pain, arrest vomiting by warming the stomach, and to relieve asthma (Anon., 1995a). High-grade agarwood powder is prescribed in Chinese medicine (Yaacob, 1999) and is also used in the production of pharmaceutical tinctures (Heuveling van Beek and Phillips, 1999). Burkill, 1966 reported that Malaysians used agarwood mixed with coconut oil as a liniment, and also in a boiled concoction to treat rheumatism and other body pain.

Bull 1930, cited in Chakrabarty et al., 1994 that Agarwood is use as a complex ointment for smallpox and for various abdominal complaints. It is also prescribed for dropsy, as a carminative, a stimulant, for heart palpitations, and as a tonic taken particularly during pregnancy, after childbirth and for diseases of female genital organs (Chakrabarty et al., 1994). By Burkill 1966, and Okugawa et al., 1993, it have been said that gaharu is also believed to have tonic and therapeutic properties which can cure rheumatism, shortness of breath, general pains, diarrhea, asthma and a lot more.

2.1.4.2 Perfume

The use of agarwood for perfumery extends back several thousands of years, and is referenced, for example, in the Old Testament several times using the term 'aloes'. Both agarwood smoke and oil are customarily used as perfume in the Middle East (Chakrabarty et al., 1994). It is also used in Arabic countries as well, where it is in high demand. Unlike many industrial perfumes, the agarwood oil is suitable for hot climates. It is by far the most precious essential oil with prices reaching as much as ten times that of sandalwood oil.

In spite of its unique qualities though, Agarwood is rarely used in European perfumeries because of its cost and good quality synthetic substitutes are yet to be created. Agarwood perfumes are seldom pure agarwood oil, but instead use an alcoholic or non-alcoholic carrier, such as sandalwood oil. The cheapest agarwood perfumes are either synthetic or a blend of oils, each with different qualities and fragrances. Although there are several commercially available synthetic agarwood fragrance compounds, they can produce only low-quality agarwood fragrances, owing to the chemical structure of natural oil (Heuveling van Beek and Phillips, 1999).

Agarwood essences have recently been used as a fragrance in soaps and shampoos (Kadir et al., 1997), cited in Schippmann, 1999. Agarwood is said to have been highly prized by European perfumers in the mid-1990s (cited in Chakrabarty et al., 1994).

(Figure 2.2: Gaharu Technologies, 2011)

2.1.4.3 Incense

Irregular chunks of agarwood usually a few centimeters long and weighing 10-200 g, may be cut or broken into smaller pieces and then burned, usually in a specially made incense burner (Heuveling van Beek and Phillips, 1999). In Middle East, the Egyptians are believed to have used agarwood incense as part of their death rituals more than 3,000 years ago (Person, 2009). It is also used for various purposes in the Middle East, especially

during prayers (Yaacob, 1999). In Japan, a revival in the ancient art of Koh doh, the incense ceremony, has revitalized interest in agarwood (Katz, 1996).

The Taiwanese consumers purchase agarwood for the manufacture of incense sticks, which are used in Agarwood perfume, chips and powder and use it in prayers during many traditional festivals and ceremonies to bring safety and good luck (TRAFFIC East Asia-Taipei, in litt. to TRAFFIC International, 2 May 2000) In Malaysia, Muslims burn agarwood splinters or chips to produce incense during special religious occasions, particularly at gatherings, and agarwood incense has been recorded in use there during Ramadan prayers (Chakrabarty et al., 1994). Some Malay tribes fumigate paddy fields with agarwood smoke to appease local spirits (Chakrabarty et al., 1994).

2.1.4.4 Others

Burkill, 1966 reported that grated agarwood has also used in Malaysia for cosmetic purposes. Twine is reported to be made from Aquilaria in Malacca, a province of Malaysia (Chakrabarty et al., 1994). The use of agarwood bark as a writing material has also been documented extensively and agarwood is used for chronicles of important and sacred religious books. The use of gaharu wood as a substitute for paper is also known from the mountaineers of Annam (Vietnam) and from China (Chakrabarty et al., 1994).

Aquilaria bark was reportedly used for this purpose during the nineteenth century (Heuveling van Beek and Phillips, 1999). Some foresters in India have suggested using Aquilaria wood for constructing tea-boxes (Chakrabarty et al., 1994). There are a considerable number of craft shops offering religious ‘agarwood’ sculptures, usually Buddhist figures. Although a proportion of immature agarwood is used in this trade, most statues are not made with agarwood, owing to its soft and flaky properties, which make it unsuitable for carving. Solid pieces of agarwood are highly appreciated as ‘natural art’ in Japan, Korea and Taiwan. Craftsmen carve raw pieces of agarwood into beautiful wooden sculptures. Moreover, agarwood is also turned into beads and bracelets (Person, 2009).

2.2 ESSENTIAL OIL

2.2.1 About essential oil

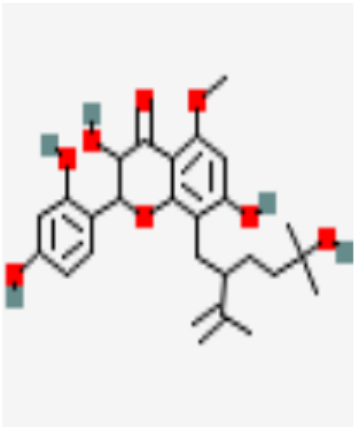
Essential oils, like all organic compounds, are made up of hydrocarbon molecules and can further be classified as terpenes, alcohols, esters, aldehydes, ketones and phenols etc (Nor Azah Mohd Ali, 2002). The terpenes in Gaharu oil can be further divided into monoterpenes and sesquiterpenes. Most monoterpenes in Gaharu oil have a structure consisting 10 carbon atoms and at least one double bond. Terpenes react readily with air in the presence of even the smallest heat source. This is the reason citrus oils degrade quickly unless properly stored. Sesquiterpenes on the other hand consist of 15 carbon atoms and have complex pharmacological actions which include anti-inflammatory and anti-allergy properties. Professor Otto Wallach attributes the fragrance of Gaharu oil mostly to the presence of terpenes and cites the terpenes as having greatly influenced the oil industry. In addition, for oxygenated compounds, they are contains phenols and alcohols such as monoterpene and sesquiterpene alcohol. The phenols found in essential oils normally have a carbon side chain and here we can look at compounds such as thymol, eugenol and carvacrol. These components have great antiseptic, antibacterial and disinfectant qualities and also have greatly stimulating therapeutic properties.

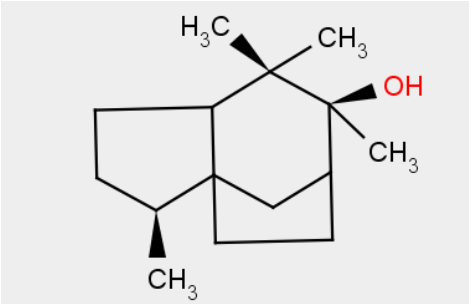
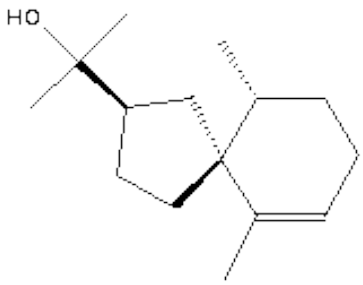
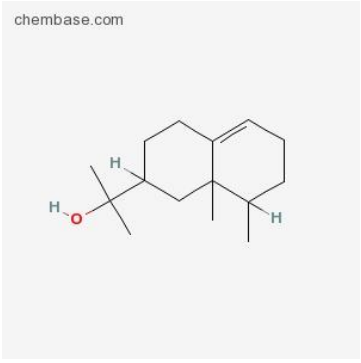
2.2.2 Chemical components

Some of important compounds of gaharu are agarospirol, jinkohol-eremol, jinkohol and kusenol which contribute to the characteristic aroma of gaharu (Nakanishi et al., 1984, Ishihara et al., 1993). Specifically the chemical compounds of interest discovered in Aquilaria Malaccensis Benth are α-agarofuran, 10-epi-γ-eudesmol 6.2%, agarospirol 7.2%, jinkohol 5.2%, jinko-eremol 3.7%, khusenol 3.4%, jinkohol II 5.6%, and oxoagarospirol

3.1% (Yoneda et al, 1984, Nakanishi et al, 1984) but in generally, gaharu oils are mixture of sesquiterpenes, sesquiterpene alcohols, oxygenated compounds, chromone derivatives and resins. Other compounds such as 2-(2-4'-methoxyphenylethyl) chromone also produce a long lasting fragrance upon burning.

Table 2.4: Chemical constituent in gaharu (Pubchem, 2005)

Chemical constituent in gaharu	**IUPAC name/molecular formula**	**Molecular weight(MW)**
Khusenol	2-(2,4-dihydroxyphenyl)-3,7-dihydroxy-8-(5--elicoid-5-methyl-2-prop-1-en-2-yl-hexyl)-5-methoxy-chroman-4-one 	472.527 g/mol

Jinkohol	C15H26O  (tcm.cmu.edu.tw, *n.d.*)	222.366 g/mol
Agarospirol	2-(6,10-dimethyl-2-spiro[4.5]dec-9- enyl)propan-2-ol  (Caslab.com,*n.d.)*	222.366 g/mol
Jinkoheremol	2-(8,8a-dimethyl-2,3,4,6,7,8-hexahydro-1H-elicoids-e-2-yl)propan-2-ol  (Chembase.com,*n.d.)*	222.366 g/mol

2.3 EXTRACTION

2.3.1 Types

Extraction is a separation process to separate the desired product solute and/or to removed undesired solute compound from the solid where the solid is contacted with a liquid phase. There are many equipment have been develop and build for the purpose of extraction. This section will discuss more on the types of extraction equipment such as microwave assisted extraction (MAE) , steam distillation and supercritical fluid extraction method(SFCE).

2.3.2 Microwave Assisted Extraction (MAE)

Microwave assisted extraction (MAE) is based on the direct application of electromagnetic radiation to a material. It has an ability to absorb electromagnetic energy and to transform it into heat. Unlike conventional heating by infrared energy or thermal conductivity, the increase in temperature occurs simultaneously in the whole volume of solvent. This process is caused by the multiple collisions of the solvent molecules as they realign in the oscillating electromagnetic field, which generates energy in the form of heat. Compared with other extraction methods such as ultrasonic extraction and Soxhlet extraction, MAE are reported to be a higher recovery of the analyte, shorter extraction times and the use of smaller quantities of solvent. In open systems, the extraction occurs at atmospheric pressure and with variable energy input. In closed systems, extraction takes place at controlled pressure, up to 5 atm and a temperature that may exceed the boiling point of the solvent under atmospheric conditions, to increase extraction efficiency.

There are many factors affecting the efficiency of microwave extraction. Solvent used, time of application of microwave, microwave power level, and temperature are the